

# Polarized Ca XANES and EXAFS studies of minerals

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## INTRODUCTION

Ca is an important ion in a huge number of mineralogical, agricultural, biochemical and environmental systems. In many of these systems it is the main constituent of important compounds, crystals, proteins or functional units. In other cases it is a very important minor or trace element. Additionally, Ca aqueous chemistry plays a vital role in soil and aquatic chemical cycles, and several of its common precipitating phases in soils are significant environmental remediation agents (e.g., apatite and ettringite). Finally, calcium plays a vital role in human biochemistry, associated with protein formation, as a cofactor for enzymes, in bone and tooth growth and as a chemical regulator [1,2]. Ca may have coordination environments with from 4 to 12 nearest neighbors including OH, F, Cl, O, OH<sub>2</sub>, NH<sub>3</sub>, and Br ligands. Spectral characterization allowing identification of Ca phase, crystallographic site, bonding distances or ligand type is especially relevant to many kinds of biogeochemical investigations, but has been little attempted [3,4]. Additionally, Ca has an empty 3d shell, and thus is a good candidate for x-ray spectra simulation especially at the 2p (L<sub>2,3</sub>) edge. We have been able to collect high quality 2p and 1s XANES spectra, in addition to 1s EXAFS, both in powder and single crystal mode. All 2p work was done on ALS beamline 9.3.2, while 1s edge studies were done on ALS beamline 9.3.1.

## RESULTS

Figure 1 shows an EXAFS scan from ALS beamline 9.3.1 over the Ca K edge for a single crystal of the tetragonal mineral apophyllite. The electric vector is polarized in the crystallographic <010> direction. Right insert shows the polarization dependence of the K-edge XANES structure. Left insert shows the transformed EXAFS correlation functions for the two polarization directions. In the <001> orientation Ca-Ca and Ca-K correlations at distances from 4-5 Å (uncorrected for phase shifts) do not appear. Changes in contributions from Ca-Si correlations affect the second shell structure in the <001> orientation. The structure model on the right with <001> direction vertical shows the positions of Si (red) and O (blue-green) about Ca (brown). The violet-blue atom is F. Spectra were obtained for a set of 12 minerals, each having different Ca local environments. Polarized spectral data was obtained for 6 species on the K-edge. (There can be little polarization dependence on the L<sub>2,3</sub> edge spectra.)

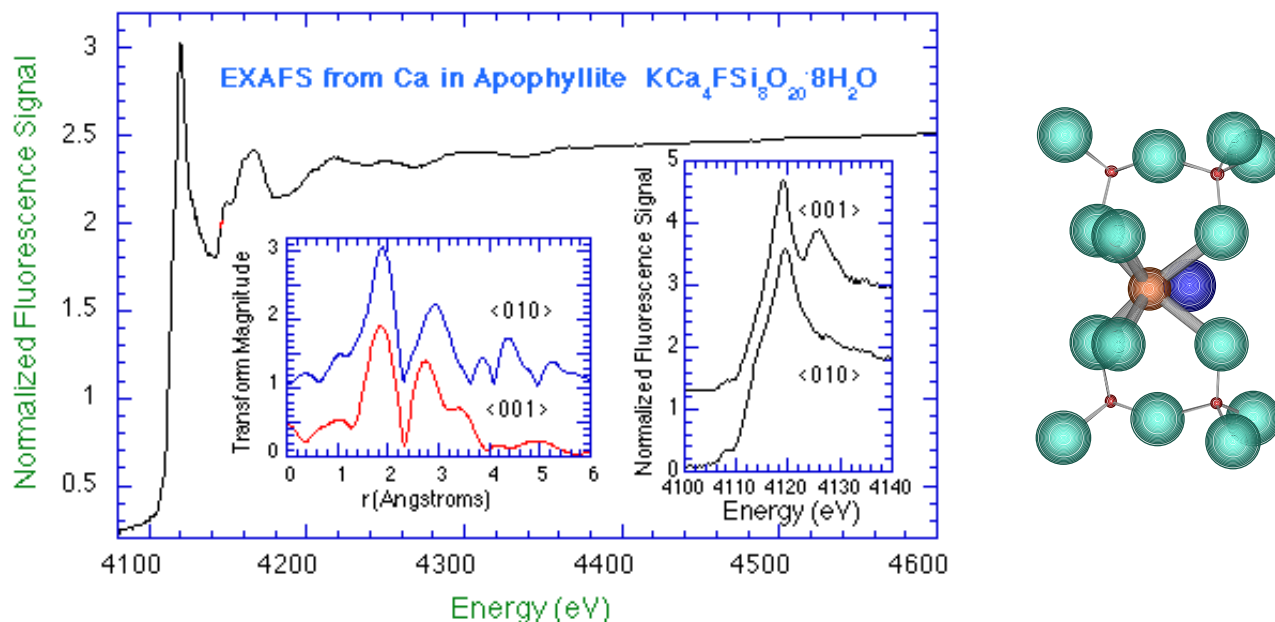


Fig. 1. Polarized EXAFS and XANES at the Ca K edge. Beamline 9.3.1  
Model on the right shows the Ca environment in apophyllite (<001> vertical).

Figure 2 shows a comparison of  $L_{2,3}$  XANES spectra for several Ca minerals. The differences are due largely to variations in the local crystal field about the Ca. The features appearing from 355.5 to 357.5 eV are due to Fe in the samples and second harmonic contamination in the incident beam. Simulations of these spectra with the program TT Multiplets [5] are in progress. Simulations of the K-edge XANES are being done with Feff 8.0x self-consistent potential full multiple scattering calculations [6]. All work on these materials was done under UHV conditions using a channeltron to detect total electron yield. However future studies are planned for aqueous-containing environments utilizing fluorescence detection and He-H<sub>2</sub>O atmospheres to emulate environmental and biological conditions.

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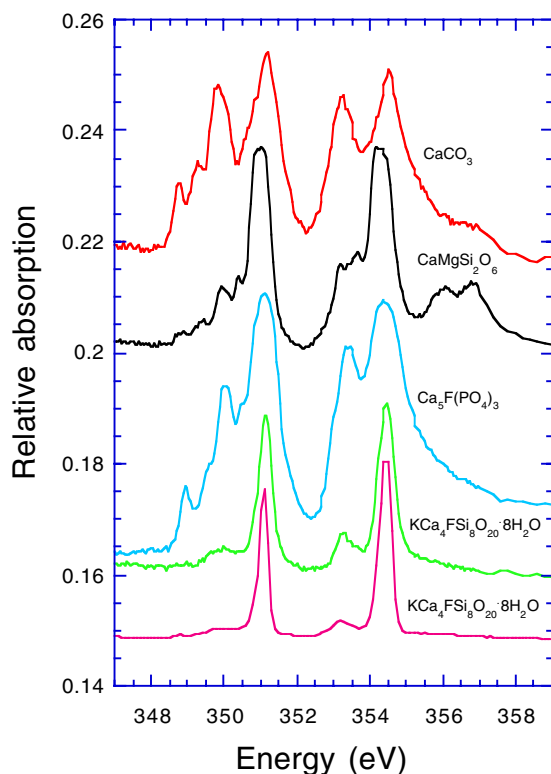


Fig. 2 Comparison of Ca 2p ( $L_{2,3}$ ) XANES from mineral structures. From bottom: apophyllite e-vector along  $\langle 001 \rangle$  [7], apophyllite powder [7], apatite [7 and 9], diopside [8] and calcite [6], where [n] indicates Ca-X first neighbor coordination numbers.

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